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INVESTIGATION OF KINETICS OF ISO-OCTANE IGNITION UNDER SCRAMJET CONDITIONS (POSTPRINT)

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14. ABSTRACT

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Investigation of Kinetics of Iso-Octane Ignition under Scramjet Conditions

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ABSTRACT: A single pulse reflected shock tube was used to investigate iso-octane ignition over the temperature range of 900–1400 K at a pressure of ∼1 atm. To account for the anticipated long ignition delay times at the lower temperatures, long shock tube dwell times (∼12 ms) at lower temperature and near atmospheric pressure were achieved by using argon–helium mix as a driver gas. Chemical thermometer experiments were conducted to remove any uncertainties in determining postreflected shock temperatures. The ignition delay data obtained in this study are in good agreement (in the overlap region) with the iso-octane ignition data from a previous shock tube study. However, the activation energy of iso-octane ignition obtained in this study in the lower temperature region (<1300 K) is significantly smaller (∼15 kcal vs. ∼40 kcal) than that obtained in a previous higher temperature study. The deflagration may be responsible for lowering of activation energy under the conditions of this study. Two detailed iso-octane kinetic models (Air Force Research Laboratory—AFRL and Curran et al.) were used to model the experimental results of this study. The AFRL mechanism showed a good agreement with the experimental iso-octane ignition delays and their temperature dependence. © 2006 Wiley Periodicals, Inc. Int J Chem Kinet 38: 194–201, 2006

INTRODUCTION

Several researchers have pointed out that a fundamental understanding of detailed combustion chemistry is necessary for the development of hydrocarbon-fueled advanced airbreathing propulsion systems [1,2]. A notable example is the rocket-based combined cycle (RBCC) engine being developed for earth-to-orbit reusable launch vehicles which integrates an air-

augmented rocket, a ramjet, and a supersonic combustion ramjet (scramjet) into a single system [3]. Airbreathing propulsion at RBCC velocities is subject to the stressing requirement where mixing, ignition, and combustion must take place on very rapid time scales. In terms of combustion performance, the candidate hydrocarbon fuel should mix and react (to near completion) in the span of about 1 ms, a typical combustor residence time. Unfortunately, scramjet combustor inlet conditions, for example at the Mach-4 condition static temperature and pressure of ∼500 K and ∼1 atm (or below) [4], are not conducive to rapid reaction. A number of methods for combustion enhancement have thus been suggested and explored

to varying degrees. Hot gas piloting, photo irradiation, energy intensive ignition sources (e.g., laser, plasma), heterogeneous catalysts, and homogeneous catalysts are typical of the techniques that have been considered for combustion enhancement, particularly under conditions where ignition would not otherwise occur. However, a major hurdle for success of any combustion enhancement technique is the lack of combustion data at conditions relevant to scramjet operations.

One motivation for this study was to provide ignition data for a hydrocarbon fuel at conditions relevant to scramjet operation and to provide a database against which to compare and validate a recently assembled kinetics mechanism, the AFRL Mech.

Iso-octane (2,2,4-trimethylpentane) was chosen as a fuel for this study because it is a primary reference fuel and also a major constituent of surrogate JP fuels [5]. Iso-octane ignition has been studied using a jet-stirred reactor, a rapid compression machine, and shock tubes [6–10]. There is also a turbulent reactor study reported in the literature at conditions of 1080 K and 1 atm [11]. Most of the available iso-octane experimental ignition data was collected at higher pressures (4–40 atm). Only recently have shock-tube data been collected near atmospheric pressures (and at temperatures from ~1200 to 2000 K), and while these data are useful, it is necessary to extend the temperature range to lower values [6]. Thus, additional studies were initiated consisting of both shock tube experiments to measure ignition delay times and kinetic modeling to help identify promising points of attack in the combustion chemistry.

The shock tube experiments are technically challenging due to the need to create stable gas mixtures containing condensable components. These experiments were performed in a high-purity, turbo-pumped single-pulse reflected shock tube located at the University of Dayton. The shock tube has been successfully used in the past to measure ignition characteristics of hydrocarbon fuels [6,7,12]. The major advantage of using the shock tube is that main combustion parameters like temperature, pressure, equivalence ratio, and fuel composition can be varied independently. Also, compression by shock waves is fast enough to avoid any influence of the compression process on the ignition behavior. The study presented here was conducted at postreflected shock pressures of ~1 atm and covers a temperature range from 900 to 1400 K. While this range does not extend to the lowest temperatures of interest to scramjet engine start-up scenarios (~600 K), it does extend the available database to temperatures lower than were previously available.

EXPERIMENTAL

A single pulse reflected shock tube was used for all experiments. The shock tube is composed of a 7.6 cm ID × 274 cm long driver section, a 5.08 cm ID × 275 cm long driven section, and a 61 cm long square (4.5 cm × 4.5 cm—inside) test section. A square cross section design of test sections allows for four fused-silica windows with clear aperture of 5.7 cm × 1.9 cm to be placed 3 cm from end plate. The end plate was also designed with a flat window that spans the entire width and height of the test section. The test section also has six physical access ports for piezo-electric pressure transducers, gas purge lines, sample injectors, samplers, and other auxiliary equipment. It also includes a 30.5 cm ID × 61 cm long dump tank and an evacuation subsystem. To ensure that the shock wave generated in the driven section is not distorted, the optical test section was designed with the same cross-sectional area as the driven section. Furthermore, a constant-area adapter was used to transition from the circular cross section of the driven section to the square cross section of the optical test section in a flow path that has a constant cross section along its entire length. The driven and test sections are connected through a pneumatic ball valve which is controlled through the system's automatic digital firing system. A dump tank is connected to the system through a manually operated ball valve. The entire structure is made from 1.27 cm thick, type-304 stainless steel. Figure 1 shows a general schematic of the University of Dayton shock tube as used in this study.

The reaction mixture in the test section consisted of 80% argon with the balance a stoichiometric mixture of oxygen and iso-octane (2,2,4-trimethyl pentane). Initial exploratory experiments showed that with helium as driver gas it was possible to establish the required postshock pressure and temperature conditions but the dwell time was only 2 to 3 ms. This was considered far too short for the planned tests as ignition delays on the order of 5–10 ms were anticipated. The dwell time is determined by the interval from the moment the reflected shock departs the end plate (generating the shock-heated environment) to the moment the rarefaction wave arrives from the far end of the shock tube, quenching the shock-heated gas back down to low temperatures and pressures. This interval is often increased by increasing the length of the driver section, which increases the distance the rarefaction wave must traverse before arriving at the end plate and thereby delaying its arrival. Since the driver section on the Dayton shock tube is already quite long (~3 m), this was
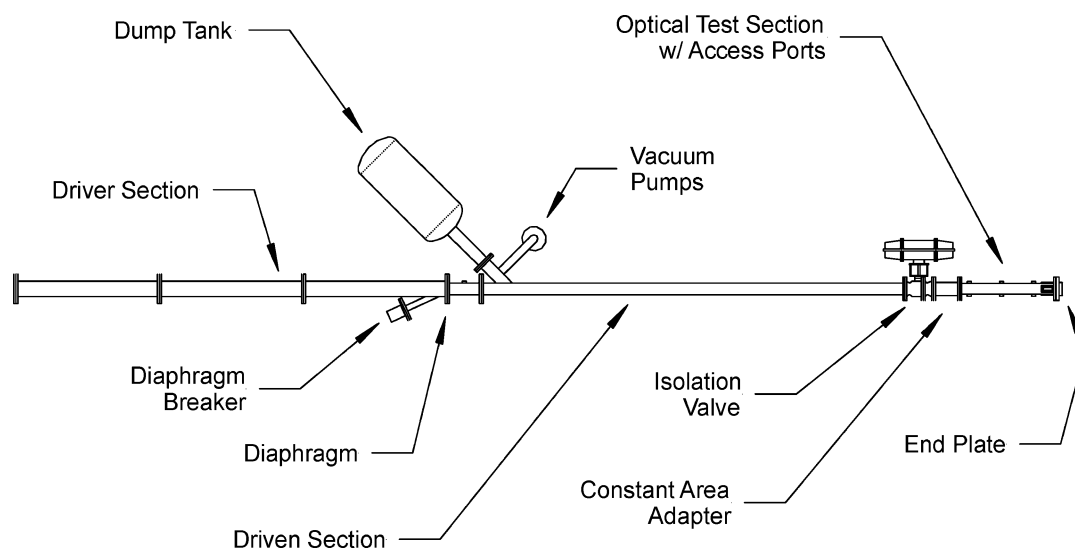
Figure 1   Schematic of the University of Dayton shock tube.

not considered a viable option given the significant increase in dwell time that was needed. An alternative solution was devised to slow the flight speed of the rarefaction wave by using a mixture of helium and argon as the driver gas. Under typical ambient conditions, helium has a speed of sound of approximately 1062 m/s while argon has a speed of sound of only 321 m/s, so mixing these two gases provides an effective means of controlling the speed of the rarefaction wave as long as the shock strength can be maintained. This approach was used in this study. Dwell times up to 12 ms were therefore possible while meeting the desired conditions of temperature and pressure when helium/argon mixes with up to 40% argon were used as driver gas. One possible drawback of this approach is that acoustic impedances of driver and driven gases will not match, which in turn can cause reflection from driver/driven gas interface to the end of the tube [13].

To eliminate uncertainties when determining postreflected shock temperatures due to nonidealities from the shock waves generated, necessary temperature calibrations were performed by way of chemical thermometer experiments. Chemical thermometers have been used extensively as both internal and external thermometers by researchers and are necessary especially during kinetic studies to obtain accurate postshock temperatures in shock tubes [14,15]. For the temperature calibrations, 1,1,1-trifluoroethylene, 1-chloropropane, and 2-chloropropane were used as external chemical thermometers. The chemical thermometers used here are known to react with hydrocarbon fuels and therefore external calibrations were performed to prevent any impact on the ignition delay that may arise by introducing the chemicals internally. Although the use of

external thermometers prevents cross-reaction, the use of external thermometers requires that the experimental variations between the calibration experiments and actual test conditions be minimized. Therefore, the calibrations were performed by substituting the oxygen and fuel content in the predetermined experimental conditions used in this study with nitrogen and the chemical thermometer while keeping the amount of diluent gas-argon fixed. Depending on the anticipated temperature conditions and the detection limit of the instrument used to analyze the test gas mixture before and after an experiment, the required amount of the chemical thermometer was introduced into the test section with the isolation valve closed. The concentration of chemical thermometer in the test section was monitored using a manometer. After the desired chemical thermometer mix was prepared, it was then exposed to the shock by opening the isolation valve immediately before firing the shock and closing it a fraction of a second later. The fraction of the chemical thermometer species remaining in the test section was determined by purging the test section after each experiment into a 25-L sample bag and analyzing using gas chromatography and mass spectrometry. Carbon tetrachloride and benzyl chloride were added into the sample bag as internal standards to account for variations in dilution when purging the test gas. Measuring the reactant concentration eliminated any uncertainties associated with measuring product concentrations resulting from potential secondary reactions of product species. The average postshock temperatures were obtained by using Eq. (1)

$$T = \frac{(-E/R)}{\ln\{\ln(1/x)/(A \times t)\}} \qquad (1)$$

where the fraction remaining is $x = CT_{Final}/CT_{Initial}$ (the ratio of the final to initial concentration of the chemical thermometer), t is the dwell time (reaction time) measured using the end-plate pressure transducer, R is the gas constant, and A and E are the Arrhenius pre-exponential factor and activation energy, respectively, both obtained from the literature [15,16]. The temperatures obtained from chemical thermometer experiments were then used to calibrate temperatures that were calculated based on shock velocities. The range of shock conditions used in this study was covered using three different chemical thermometers. The chemical thermometer experiments were conducted at close temperature intervals, and gas chromatography measurements were repeated to minimize and quantify inherent experimental scatter (±4 K).

For iso-octane experiments, the fuel mixture was prepared in a silicosteel mixing bulb and then injected into the test section. The mixture was prepared by injecting 17.3 Torr of iso-octane followed by 932.7 Torr of argon measured using a 1000-Torr capacitance manometer with a readout precision of 0.1 Torr. All surfaces were passivated three times before each shock tube measurement. After the shock tube had been passivated and filled, the oxygen was injected to produce a stoichiometric fuel–air mixture just prior to firing the shock tube. Immediately before the diaphragm is ruptured, the ball valve is opened and the test gas is exposed to the shock. The incident velocity was measured by dividing the distance by the arrival time of the shock, as determined by piezoelectric pressure transducers mounted on the sidewall (35.5 cm from the end plate) and the end plate. This derived incident shock velocity was then used to calculate conditions in the test section using a model based on an algorithm developed by Gardiner et al. [17] and data from the JANAF tables. The temperatures thus calculated were then calibrated using chemical thermometer data. Two photodetectors were employed to capture the emission from the ignition event: a photomultiplier tube (PMT), fitted with a 10-nm bandpass interference filter centered at 430 nm (along with neutral density filters to attenuate the signal and maintain linear behavior), for detection of CH A-X chemiluminescence, and a large-area, amplified photodiode (1 MHz bandwidth), for detection of visible broadband emission. Note that OH A-X chemiluminescence (isolated with a 310-nm interference filter) yielded the same result as CH emission. Both photodetectors viewed emission through the fused-silica windows at a distance of ~7 cm from the end plate of the shock tube. The ignition delay times were determined with the optical sensor data and the data from the pressure transducers. All pressure events were sampled at 250 kHz using a digital oscilloscope.

RESULTS AND DISCUSSION

In this study iso-octane ignition delays were measured at a pressure of ~1 atm and for combustion temperatures (postreflected shock) ranging from 900 to 1400 K. After each experiment, the source data were collected from four channels of the digital oscilloscope. Two oscilloscope channels represent the pressure measured by the piezoelectric transducers at the sidewall of the test section and at the end plate. These traces show when the incident shock reaches each pressure transducer, thus providing a means of calculating the incident shock velocity as well as the pressure rise associated with the ignition of the mixture.

The end-plate pressure transducer was used to measure ignition delays as it represents the origin of the reflected shock and the earliest creation of the shock-heated conditions. Specifically, the ignition delay was taken as the time interval from the moment the incident shock arrives (and simultaneously departs) at the end plate to the moment the pressure rise associated with ignition is observed. The other two channels of oscilloscope represent the PMT and photodiode data. Figure 2 shows a sample oscilloscope trace with all four channels of data. A close examination of the end-plate pressure transducer trace in Fig. 2 shows that reflection of the shock front at the end plate generates the desired temperature conditions (T5) at a pressure of ~1 atm. The pressure trace then stays flat for about 2 ms, and then there is another increase followed by a gentle rise which is then followed by a peak in the pressure trace. The increase in pressure following shock reflection is probably due to reflection from the contact surface (interface between driver and driven gases) [13]. The gentle rise after contact surface reflection is due, presumably, to deflagration, which has been observed
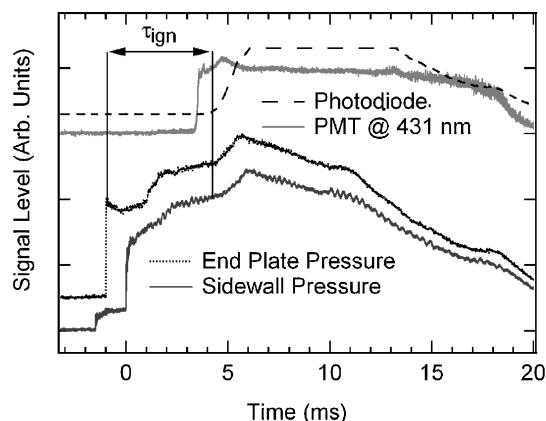

Figure 2 An example oscilloscope trace from iso-octane experiment showing pressure transducers, PMT, and photodiode data at corrected T5 = 928 K and P5 = 1.01 atm.

in a previous study of iso-octane ignition [7]. The deflagration was also observed visually when selected iso-octane experiments were filmed using a high speed camera (FASTCAM-Ultima APX – 10,000 frames/s) located at the end-plate window. The advent of deflagration coincides with the rise in CH-band emission (PMT channel) at ~4.5 ms. The CH emission from the A electronic state is characteristic of deflagration and is not an autoignition event in cases where deflagration leads to autoignition. In Fig. 2, the sharp rise in CH at ~4.5 ms is presumably from deflagration, and later the modest additional rise in PMT signal from autoignition. The rapid rise in pressure signifies a homogenous ignition (detonation), and its start is consistent with the rise in photodiode signal and peak in the CH emission trace. Examination of oscilloscope traces of all experiments showed that the start of pressure peak due to ignition was consistent with the rise in the photodiode and the peak CH emission signals. Since the photodiode signal produces the sharpest signature in time, the ignition delay times (τ_{ign}) in this study were taken as the time interval from the moment the shock was reflected at the end plate to the moment the photodiode signal rise was observed.

The origin and magnitude of the first increase in P5 (and thus T5) needs to be determined before the ignition delay data from this study can be modeled or compared to data from other iso-octane ignition studies, i.e., confirm that this rise is not associated with any combustion related events. To accomplish this task, selected experiments were repeated without any iso-octane in the test section. Oxygen was used to make up the small fraction of iso-octane (1.48%), and the tested mixtures were 80% argon and 20% oxygen. Figure 3 shows a sample oscilloscope trace from these experiments. PMT and photodiode traces are missing from
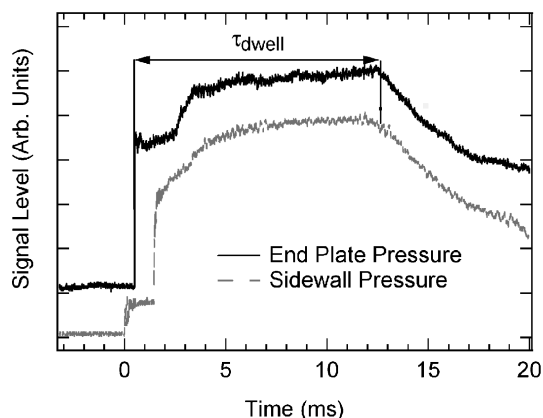
Fig. 3 as no iso-octane was present in these experiments. Figure 3 clearly shows an increase in P5 (and T5) due to reflection from contact surface. This suggests that the increase in P5 (and T5) is a gasdynamic phenomenon which is perhaps a result of interactions between shockwave and boundary layer and/or due to mismatch in acoustic impedances of driver and driven gas. In either case, this first rise is a gasdynamic effect that is also present in the chemical thermometer experiments. It follows that the temperature obtained from the chemical thermometer accounts for this increase in P5 and T5 and can be used to obtain the average temperature over the extended dwell time (~11 ms). In other words, the temperature obtained from the chemical thermometer experiments is the average temperature that the chemical thermometer experienced during the complete reaction (dwell) time. Therefore, when the calculated postreflected shock temperatures are corrected based on chemical thermometer data, the correction is accounting for the increase in P5 and T5 due to reflection from the contact surface. Besides the temperature effects caused by the reflected shock and contact surface interactions, other nonideal gasdynamic effects like boundary-layer interactions are also responsible for observed difference between the calculated temperature and the actual temperature experienced by the test gas. The temperature difference increases with increase in shock velocity. The temperature difference—ΔT, between the value given by the chemical thermometer and the initial value derived from the shock velocity—is ~1 K at the lowest temperature (916 K) and ~200 K at the highest temperature (1396 K) investigated. This increase in ΔT with increasing temperature can be attributed to an increase in nonidealities caused by boundary-layer interactions, and the use of chemical thermometers accounts for these temperature nonhomogeneities as well. Table I shows all the iso-octane ignition data collected in this study with P5 (postreflected shock pressures) and the chemically corrected postreflected shock temperatures T5.

The shock tube iso-octane ignition delay data thus obtained was modeled using the CHEMKIN software series and compared against the experimental data (see Fig. 4). Two iso-octane kinetic mechanisms were used, one by Curran et al. [18] and the other developed at the Air Force Research Laboratory (AFRL). Other iso-octane kinetic mechanisms (e.g., those of Davis and Law [19], Pitsch et al. [20], and Ranzi et al. [21]) are available in the literature and were used by Oehlschlaeger et al. to fit their iso-octane ignition data [6]. Oehlschlaeger et al. found that all these iso-octane models (including one by Curran et al.) were able to predict ignition delay within factor of two but were not able to capture the temperature dependence

Figure 3 An example oscilloscope trace from argon–oxygen only experiment showing pressure transducer data at corrected T5 = 1001 K and P5 = 0.94 atm.

Table I Experimental Iso-octane Ignition Delay Data

Chemically Corrected Postreflected Shock Temperature T5 (K)	Postreflected Shock Pressure P5 (atm)	Ignition Delay τ_{ign} (ms)
916	0.98	5.970
926	1.00	5.600
928	1.01	5.380
931	0.99	5.400
945	0.95	3.380
948	0.99	4.000
968	1.03	3.310
976	1.02	3.090
981	1.01	2.960
1003	1.04	2.600
1007	1.06	2.480
1023	1.06	2.130
1042	1.09	1.820
1053	1.07	1.650
1071	1.03	1.440
1074	1.13	1.390
1085	1.11	1.470
1090	0.99	1.290
1113	0.99	1.070
1125	0.92	1.020
1155	0.92	0.896
1165	0.91	0.674
1169	0.95	0.642
1180	0.94	0.718
1196	0.97	0.645
1218	0.98	0.631
1227	1.02	0.557
1239	0.95	0.500
1257	0.91	0.476
1261	0.95	0.457
1270	0.93	0.448
1299	0.98	0.401
1329	0.95	0.275
1362	0.91	0.200
1396	0.96	0.165

Figure 4 Comparison of iso-octane ignition delay times (τ_{ign}) from this study (Dayton data) with that obtained in Oehlschlaeger et al. study (Stanford data) [6]. Solid squares are Dayton ignition delays versus chemically corrected post-shock temperature (T5); and solid circles are Stanford ignition delays. The solid line depicts the AFRL mechanism, and the dashed line depicts results from the mechanism of Curran et al. [18].

to model iso-octane combustion. The complete mechanism is available upon request. As shown in Fig. 5, the AFRL mechanism has been successfully used to model (using modified version of the CONP program of the CHEMKIN II software series), the ignition delay measurements of stoichiometric mixtures of iso-octane and air obtained in a rapid compression machine at a pressure of ~10 atm over the 900–950 K temperature range [27]. There is excellent agreement between the calculated ignition delay times and the experimentally observed values as a function of the compressed gas temperature, taken as the initial temperature in the computations. The computational results obtained using the AFRL mechanism plotted in Fig. 4 also show

exhibited by their experimental data. In this study, we decided to use only the Curran et al. model for comparison, as it was easily available on the World Wide Web in CHEMKIN format and had given comparable fits (as the other available models) to the measurements of Oehlschlaeger et al. This mechanism of Curran et al. was used in conjunction with the Shock Solution of CHEMKIN III (release 7) software series.

The other mechanism, AFRL Mech is based on the *n*-heptane mechanism developed by Maurice and coworkers [22–26] with the addition of several reactions pertaining to the combustion of branched alkanes
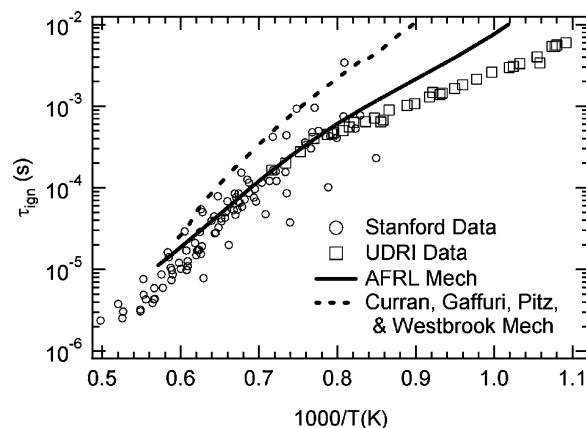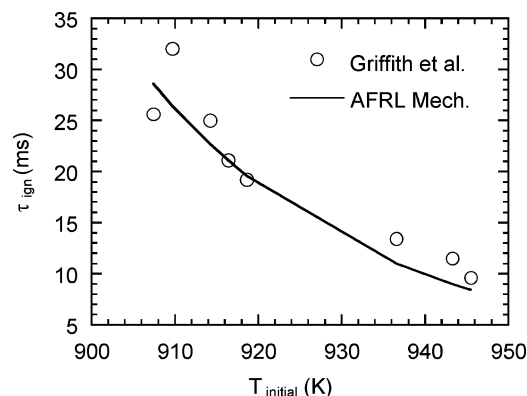

Figure 5 Ignition delay time (τ_{ign}) variation with compressed gas temperature ($T_{initial}$). The experimental data (open circles) are taken from Griffith et al. [27], and the solid line represents the AFRL iso-octane mechanism results.

good agreement with the calculated ignition delay time and the experimental iso-octane ignition delays observed in this study. For comparison, the ignition delays calculated using Curran et al. mechanism are considerably higher than those observed in this study in the low-temperature region.

Also Fig. 4 compares the iso-octane ignition data from this study with that reported in Oehlschlaeger et al. (Stanford Data) [6]. The ignition delay time data from Oehlschlaeger et al. were obtained in 95 total experiments spanning a variety of pressures, equivalence ratios, and oxygen mole fractions in addition to the temperature. These ignition times were correlated using the regression analysis given by Oehlschlaeger et al. This relation was used to normalize all of their data to our conditions of 1 atm, equivalence ratio of 1, and 18.52% oxygen mole fraction. Both the Dayton and Stanford data sets are plotted in Fig. 4 and exhibit good agreement where the two data sets overlap (1200–1400 K). The AFRL mechanism shows a better agreement with the combined data set (Dayton and Stanford data) than the mechanism by Curran et al. Comparison of Dayton and Stanford data also shows that activation energy of ignition at lower temperature (Dayton data) is significantly smaller, $\sim$15 kcal vs. $\sim$40 kcal, than that obtained at higher temperatures (Stanford data). One explanation of this disagreement is that deflagration plays a significant role in lower temperature ignition and may be responsible for lowering the activation energy.

CONCLUSIONS

Most shock tube derived ignition data are outside of the range of interest for scramjet combustor inlet conditions. Accordingly, as an initial step to improve the database for jet fuel kinetics for which alkanes are a major component, a study of iso-octane ignition at low temperatures and pressures was initiated. A shock tube study was conducted to measure ignition delay times over the temperature range from 900 to 1400 K at a pressure of $\sim$1 atm. Of course, this database serves both the purposes of understanding ignition delays at lower temperatures and of providing additional data for validating complex kinetic models. The shock tube experiments were technically challenging due to the need to achieve longer dwell times at lower temperatures and near atmospheric pressure. The experimental conditions were achieved using an argon–helium mixture as driver gas. However, this can result in reflection from contact surface and a corresponding increase in the postshock temperature (T5). This and other nonideal shock-tube behaviors were characterized using external chemical thermometers. The ignition delay data obtained in this study are in good agreement with that reported recently in the region of overlap for the two studies, 1200–1400 K. The combined data sets contain ignition delay times spanning 3 orders of magnitude (from about 5 ms to 5 μs) and temperatures ranging from 900 to 2000 K. This extensive range has allowed us to test the recently developed AFRL hydrocarbon kinetics mechanism (AFRL Mech). This mechanism shows good agreement with experimental data obtained in this study and also with the combined data set, thus providing validation (of this mechanism) as a part of an overall effort to develop accurate kinetics models of jet fuels and their surrogates.

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